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PROCESSING OF TITANIUM

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1. Introduction

For the production of titanium either the so-called Fast, Arkel, and de Boer iodide method or a modified Kroll method is used in Hungary. It is well known that titanium produced by the decomposition of titaniumtetraiodide is very pure, while titanium produced by the Kroll method or by one of its modifications always contains impurities of oxygen, hydrogen, nitrogen, and iron. The properties of the 2 types of titanium therefore cannot be considered identical either with regard to hardness or from a technological point of view. Only titanium produced by the iodide method can be considered titanium metal. Titanium produced by the Kroll method is always an alloy, at best with only very small quantities of the alloying substances.

According to expert opinions in the literature the hardness of titanium itself gives some information about the quantities of impurities it contains. Various authors have investigated the relationship between impurities and the hardness of the metal.

Figure 1, based on data by Jaffe and Campbell, illustrates t. effect of oxygen, hydrogen, nitrogen, and iron on the hardness of titanium. In the Kroll method the quantities of impurities depend very largely on the purity of materials used, on the structure of the reactor and progress of the reaction, and on the method of processing the formed titanium sponge.

For the processing of the titanium sponge today 2 methods appear to be available. One is the annealing in high vacuum of all the products in the reactor, i. e., of the titanium, the remaining magnesium, and magnesium chloride; the titanium can then be freed from excessive magnesium and magnesium chloride by means of distillation.

The other method is the wet processing method by which the magnesium chloride can be eliminated with water and the magnesium metal dissolved with dilute hydrochloric acid. Titanium produced by distillation is much purer, since titanium purified by the wet method is more apt to be contaminated with oxygen and hydrogen. The Kroll method therefore also gives us 2 qualities which must be considered after processing: titanium powder produced by the wet method and titanium sponge produced by annealing. The hardness of titanium purified by washing is 190-250 Brinell, while the hardness of vacuum distilled titanium is 130-190 depending on the purity.

The question becomes even more complicated when the quality of the titanium sponge is examined within each reaction. According to Wartmann, Baker, Nettle, and Homme 4 zones can be distinguished in the reactor (Figure 2). The purest is the No 1 section, while nos 2, 3, and 4, in that order are progressively more contaminated. The author's explanation is that the part of titanium which is in direct contact with the iron container, and the first formed titanium sponge absorb all the magnesium impurities and so the No 4 portion is generally most contaminated. This gradually diminishes through the No 3 and 2 zones toward No 1. There is a difference of almost 50 % between the hardness of the material processed from titanium sponge from zone No 1 and zone No 4.

The processing of the titanium sponge produced in the reactor can be done in 2 different ways: either the whole content of the reactor has to be homogenised during processing, which produces a medium quality; or the No 2, 3, and 4 qualities will have to be processed separately, possibly mixed with some No 1 titanium sponge to produce exactly the type of alloy required. Such separation of the sponge is only practical in case of large reactors, but for this very reason it is an important question in case of industrial production.

Titanium produced by the reactor will therefore inevitably be contaminated by gases and iron, and will have properties very different from pure titanium. Because the quantities produced by these methods are sufficiently large, it is important to consider the possibilities of their industrial use, as well as the question of the type of alloy that would be produced if the whole content of the reactor were to be processed as a homogeneous unit. As far as quality is concerned, 3 different titanium qualities can be considered depending on the method of production. In the order of diminishing purity they are the following.

1. Iodide titanium
2. No 1 quality of the Kroll reactor
3. No 2 quality of the Kroll reactor

The quality of products nos 2 and 3 will again be different regardless of whether the sponge has been processed with vacuum distillation or by washing. As a result there is a wide variety of titanium products with varying industrial possibilities between the approximate 80 B.h. of iodide titanium and the approximate 250-260 B.h. of the second quality and wet processed Kroll sponge.

All types however have one common requirement, i.e., they can be molded cold. Therefore the question arises as to how the iodide titanium and the various titanium sponges of the Kroll reactor should be processed to give them the ductility necessary for manufacturing.

Our previous experiments which were submitted to the committee of the academy in 1952, and also later data in the literature indicate that titanium of identical purity will exhibit different hardness properties depending on the degree of molding and the heat treatment to which it is subsequently subjected. Further investigation of the question will also show that hardness alone is no proof of ductility, and with proper heat treatment comparatively harder -- and therefore more contaminated -- types can be molded into very ductile material which is bound to meet industrial requirements.

In the experiments, the description of which follows, 2 types of titanium were used: one, which was produced by the iodide method, had a B.h. of about 90, while the other type, which was produced by the Kroll method, after tempering, had a B.h. of about 225.

2. Description of the experiments

The titanium sponge produced by the Kroll method was purified by washing and acid treatment from the byproducts of the reaction. The resulting titanium powder was pressed into a cylindrical steel casing with an 80 mm diameter and height of 120 mm. The mouth of the iron casing having been sealed airtight by welding it was annealed at 900° C for 2 hours and then hammered into a sheet of 20 mm thickness at the same temperature. After hot rolling the material was tempered again and the iron casing removed, whereupon the material was processed further at room temperature and at 300° C.

The titanium iodide which was in the form of a thread with a 66 mm diameter was rolled cold to a ribbon and tempered for 1 hour at 700° C.

As a result of the experiments from the above starting materials 3 sets have been prepared: Kroll-titanium rolled at room temperature, the same rolled at 300° C, and iodide titanium rolled cold. The purpose of the experiments was to determine the formation of the granules as a function of the molding temperature and the annealing temperature which followed, as well as to clarify the relations between the temperature of tempering, its duration, and the degree of the cold molding.

The measurements of granule sizes as a function of molding and tempering have always been based on 10-hours annealing periods, because experience in the production of semifinished titanium articles has taught that more than 10 hours of heating are seldom required. Photomicrographs indicate that after 10 hours recrystallisation has not yet been completed. Therefore the diagrams of Figure 3 do not show complete recrystallisation, but from a practical point of view they may give some useful information concerning conditions during industrial annealing.

Figure 3 a indicates that iodide titanium more readily tends to develop coarse granules than Kroll titanium. The granule size of Kroll titanium between 600° and 850° appears to be practically independent of the degree of temperature and molding. Stronger growth of granules is only noticeable at 900° C, at which temperature the largest size granules are visible in the areas of 5-10% cold molding.

Iodide titanium behaves substantially the same way.

Microscopic investigations at 500° and 550° indicate that 10 hours of annealing at these temperatures did not quite obliterate the original structure as can be seen in figures 4 and 5. Figure 4 was prepared after 10% cold molding and 10 hours of annealing at 500° C, while Figure 5 was prepared after 33% cold molding and 10 hours of annealing at 500° C. While in the case of 10% cold molding recrystallisation was already completed at 500° C, the 10 hours of annealing after a 35% cold molding still leave the characteristic structure of the cold molded texture. According to microscopic investigations the lower limit of recrystallization in case of 10 hours of annealing therefore lies between 550° and 600° C depending on the degree of molding.

No appreciable difference can be observed in the size of the granules between experiments molded at 300° C and at room temperature. It therefore can be established that molding performed below the lower temperature limit of recrystallisation has no effect on the size of the granules.

The dependence of the tempering temperature and time on the degree of molding for iodide-titanium and Kroll-titanium is shown in figures 6, 7, 8, and 9. While the deformation graph indicates that the tempering of iodide titanium for ½ hour between 500° and 600° results in a lowering of hardness, a considerable degree of hardness still remains in comparison with the greater molding. At 700 and 800° C considerable tempering already takes place without it being possible to attain the original condition of 90 Brinelles softness. After tempering at 900° C a definite hardening can observed.

Tempering for 10 hours yields similar results. Here also the tempering is done by annealing between 700 and 800° C, while at 900° C renewed hardening can be observed.

Tempering experiments with Kroll titanium produce similar diagrams, in which the hardness values are always higher during both ½ hour and 10 hours of tempering after annealing at 900° C, than any values measured at 700-800° C. The character of tempering of Kroll titanium summarized is shown in Figure 10. In accordance with the graphs for the determination of granule sizes, lowering of hardness starts at 550° C. At 680° C complete tempering takes place in ½ hour, while tempering at 900° C leads to increasing hardness.

It can be established therefore that for the tempering of Kroll titanium 680° C should be considered the lower temperature limit. In case of annealing above 680° C one should distinguish between tempering in the field, above the transformation temperature, or between them.

Therefore, in the following determination of data about strength and elongation we have conducted 2 kinds of heat treatments about 680° C and temperatures above the transformation. Table 1 shows the values for iodide titanium. The table gives average values of the test materials tempered after 5,15,25, and 35% cold molding. The reported data confirm the statement by Jaffe, Holden, and Ogden that the strength and limits of fluidity of pure titanium diminishes with the coarseness of granules, while the elongation increases.

Table ..

Heat Treatment	σ_B kg/sq mm	σ_F kg/sq mm	δ 5%
Measured in the condition ... phase without previous cold molding or heat treatment	36.3	28.0	19.7
After cold molding tempered for 1 hour at 750° C	35.3	27.2	19.7
After cold molding tempered at 900° C for 1 hour	36.1	23.6	32.6

The data of the Kroll titanium varied a great deal depending on the heat treatment the material received before. The original material of 225 Brinell hard[illegible] s cold rolled and tempered at any temperature above the softening point, but below the degrees between [illegible] transformation temperature gives the following average figures: σ_B = 73 kg/sq mm, σ_F = 63 kg/sq mm, δ_5 = 5.3%

Table 2.

Heat Treatment	σ_B kg/mm^3	σ_F kg/mm^2	δ 5%	HB kg/mm^2
After cold molding tempered below [illegible] transformation	63	73	5.3	225
10 hours at 750° C in vacuum	73.6	61.5	13.8	225
10 hours at 900° C in vacuum	75.5	63.6	9.5	260

Table 2 shows the experiments to reduce the nitrogen content by heating for 10 hours at 750° C and 900° C. As the table indicates continued heating in the field hardens Kroll titanium considerably and the elongation is also worse than when heated in the field. The elongation is considerably increased by heating for 10 hours in a vacuum, but this does not materially change its strength. It is interesting that the material heated for 10 hours in a vacuum at 900° C, in spite of its greater hardness shows better elongation than the material which was not subjected to such heat treatment but only to normal tempering. Materials heated in such manner for 10 hours at 750° C or 900° C, cold molded and tempered again in the field for 1 hour at 700° C, and material heated for 10 hours at 900° C, cold rolled and tempered for 1 hour at 700° C gave the following data for strength: $_F$ = 63.7 kg/sq mm, $_B$ = 78.8 kg/sq mm, = 17%
Material tempered for 10 hours at 750° C gave about the same strength data, but there was no further increase in elongation.

The described phenomenon can be explained in the following manner. Prolonged heating in a vacuum at high temperature will materially reduce the hydrogen content of titanium, and the higher the temperature and the longer the time of heating the greater will be the reduction. From an operational standpoint it is advisable to perform this heating in the field, but when it is likely that the impurities which are normally present in Kroll-titanium will go into solution, an increase of hardness and certain reduction of elongation will take place. This followed by cold molding and tempering in the field will give the best possible strength. To prove how favorable is the strength obtained in such manner it should be mentioned for the sake of comparison that the elongation of iodide titanium cold rolled to about the same strength is practically 0, while Kroll titanium which contains impurities of oxygen, nitrogen, and iron but is free of hydrogen and is heat treated in the proper manner even at a strength of 72 kg/sq mm will show an elogation of 17%.

In the experiments comparing the data for hardness and tensile strength both for iodide titanium and Kroll titanium the equation $\sigma_B = \frac{B.h.}{3}$ can be taken as a basis. As a measure of the resistance to molding the data for hardness can therefore be taken as a rough guide. The changes in hardness as functions of temperature can be seen in Figure 11. The hardness of iodide titanium as a function of temperature decreases more slowly than that of the Kroll titanium. In case of iodide titanium molding at a higher temperature therefore is not as advantageous as with Kroll titanium. The results can be summarised in as follows.

1. Bases on the submitted diagrams it can be established that, depending on the degree of purity, the most suitable temperature for tempering titanium is 680° C and the degrees between the transformation temperature. In case of unlike Kroll titanium contaminated with oxygen, nitrogen, and iron impurities iodide titanium tempering in the field will produce the best elongation data.

2. Hot molding iodide titanium does not offer any particular advantage and, in view of the oxydation at a higher temperature, cold molding is the most practical method for iodide titanium provided it followed by tempering in the field.

3. Kroll titanium definitely has to be tempered after hot molding, because during the relatively short hot molding full tempering does not take place. For the reduction of the hydrogen content the tempering should be kept at 900° C for 10 hours. This has to be followed by cold molding and afterwards by tempering at 680° C, or at the transformation temperature.

4. Since Kroll titanium is only cold molded, the dehydrogenation temperature has to be below the transformation temperature.

5. Cold molding of Kroll titanium can take place from room temperature up to the lower limit of tempering temperature. This is advisable to reduce resistance to molding; but observation has shown that in the case of articles produced by powder metallurgy the molding temperature must not be over 500° C, because of presence of magnesium, since otherwise cracks will develop. There is no such limitation for articles produced by casting.

Therefore, in summary, the heat treating and processing technology of the clean iodide titanium and the more contaminated Kroll titanium differ very considerably; while iodide titanium yields the best results when subjected to cold molding and tempering in the field, the best processing method for Kroll titanium is hot molding, dehydrogenating annealing in the field, followed by cold molding and tempering above the softening point but still in the field. If during the processing cold molding is not required the dehydrogenating annealing after the hot molding has to be done in the field.

J.Sz.Umanszkij, Ladislaw Jenicek, and N.P.Szarzsin also spoke on the subject.

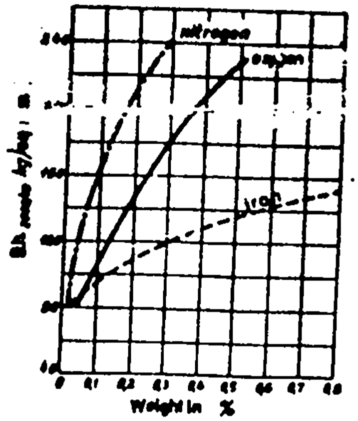

Figure 1

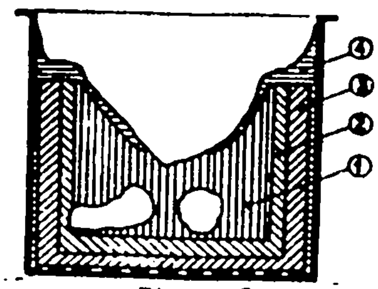

Figure 2

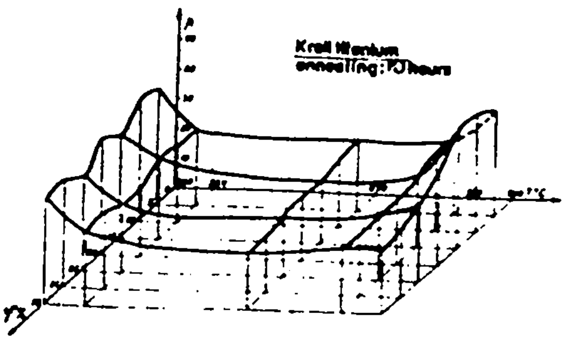

Figure 3

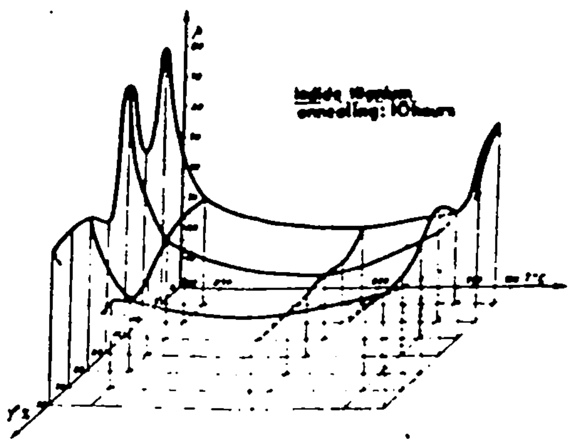

Figure 3a

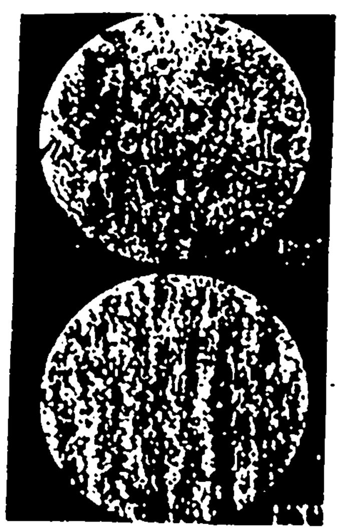

Figure 4

Figure 5

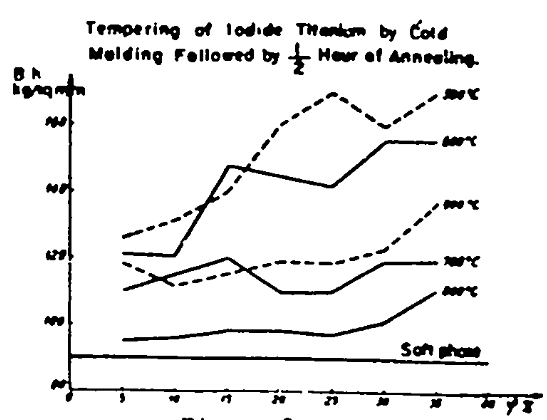

Figure 6

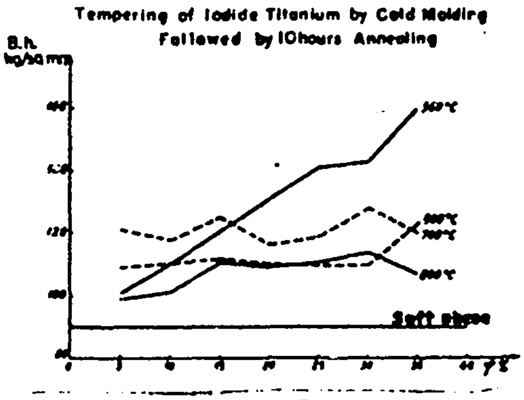

Figure 7

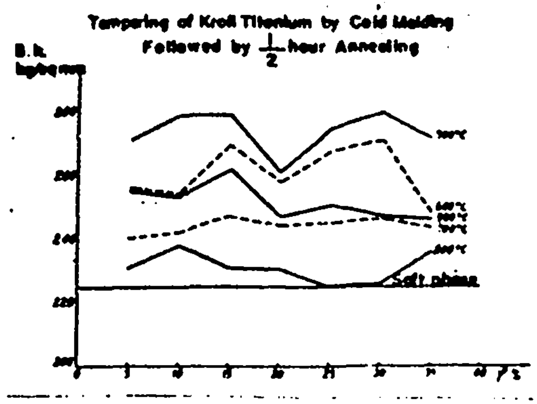

Figure 8

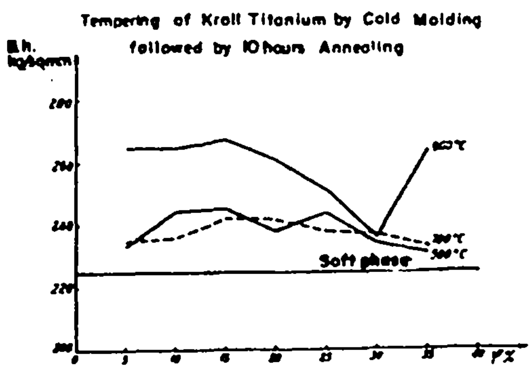

Figure 9

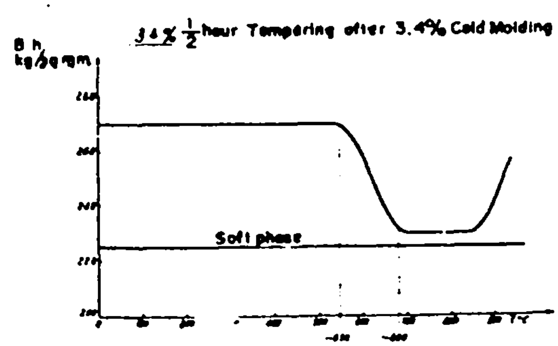

Figure 10

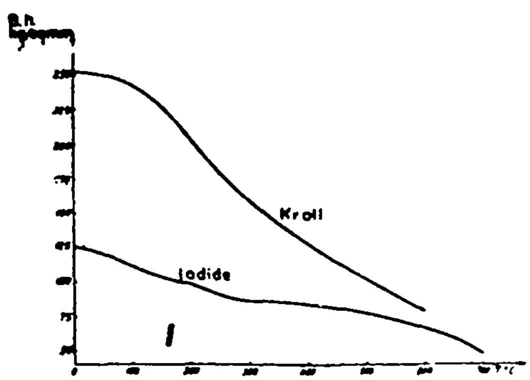

Figure 11